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(21) International Application Number: PCT/CA97/00770 (22) International Filing Date: 17 October 1997 (17.10.97) (30) Priority Data: 08/733,792 18 October 1996 (18.10.96) US (71) Applicant (for all designated States except US): McMASTER UNIVERSITY [CA/CA]; 1280 Main Street West, Hamilton, Ontario L8S 4M1 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): MIKA, Alicja, M. [PL/CA]; 25 Brodrick Street, Hamilton, Ontario L8S 3E3 (CA). CHILDS, Ronald, F. [CA/CA]; 130 Grant Boulevard, Dundas, Ontario L9H 6J4 (CA). DICKSON, James, M. [CA/CA]; 111 Hillcrest Avenue, Hamilton, Ontario L8P 2X1 (CA). (74) Agent: STEWART, Michael, I.; Sim & McBurney, 6th floor, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MICROPOROUS MEMBRANES AND USES THEREOF		
(57) Abstract Charged membranes comprise a porous substrate and a cross-linked polyelectrolyte or hydrogel located in the pores of the substrate and are useful in a variety of membrane separation processes, including pressure driven membrane separation, diffusion dialysis, Donnan dialysis, electrodialysis, electrochemical synthesis and pervaporation.		

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TITLE OF INVENTION
MICROPOROUS MEMBRANES AND USES THEREOF

5 FIELD OF INVENTION

The present invention relates to certain novel membranes and the novel uses of certain membranes.

FIELD OF INVENTION

10 This application is a continuation-in-part of US Patent Application No. 08/733,792 filed October 18, 1996.

BACKGROUND OF THE INVENTION

15 Membranes are used, for instance, in separation processes as selective barriers that allow certain chemical species to pass, i.e., the permeate, while retaining other chemical species, i.e., the retentate. Membranes are used in many applications, for example as biosensors, heparinized surfaces, facilitated transport membranes utilizing crown ethers and other carriers, targeted drug delivery systems including membrane-bound antigens, catalyst-containing membranes, treated surfaces, sharpened resolution chromatographic packing materials, narrow band optical absorbers, and in various water treatments which involve removal of a solute or contaminant, for example, dialysis, electrodialysis, microfiltration, ultrafiltration, reverse osmosis, nanofiltration and in electrolysis and in fuel cells and batteries.

20 There are a large number of supports or substrates for membranes. Specific physical and chemical characteristics to be considered when selecting a substrate include: porosity, surface area, permeability, solvent resistance, chemical stability, hydrophilicity, flexibility and mechanical integrity.

25 Other characteristics may be important in certain applications.

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In Mika et al., J. Membr. Sci., 108 (1995) pp 37 to 56, there is described a procedure for modifying microporous polypropylene and polyethylene membranes wherein 4-vinylpyridine is *in situ* polymerized into the pores of the membrane.

SUMMARY OF INVENTION

We have found that, by cross-linking the membranes described by Mika et al. with a suitable cross-linking agent, such as divinylbenzene (DVB), there are provided charged membranes comprising porous microfiltration substrate membranes whose pores have located therein a cross-linked polyelectrolyte or hydrogel anchored to the substrate polymer, which exhibit novel effects in a variety of membrane applications.

In particular, the membranes exhibit significant ion rejection properties, enabling water softening to be effected, particularly at ultra-low pressure, such as the pressure of tap water, by removing multivalent ions, such as calcium and magnesium, in preference to monovalent ions, such as sodium.

The membranes further exhibit electrochemical separator properties which make them suitable for a wide variety of applications, including electrodialysis, battery separators, fuel cell separators and electrochemical synthesis.

In addition, the membrane may be used for Donnan dialysis, diffusion dialysis and pervaporation.

Accordingly, in one aspect of the present invention, there is provided an improvement in a membrane separation process selected from the group consisting of pressure driven membrane separation, diffusion dialysis, Donnan dialysis, electrodialysis, electrochemical synthesis and pervaporation, the improvement which comprises employing a charged membrane comprising a porous substrate and a cross-linked polyelectrolyte or hydrogel located in the pores of the

substrate. Certain of the charged membranes are novel, as set forth in the claims herein and described below.

The polyelectrolyte or hydrogel may be found in the pores of the substrate by *in situ* polymerization of a monomer or a mixture of monomers with a cross-linking agent, the monomer or at least one of the monomer mixture being selected from those monomers which contain a functional group that provides an ion-exchange site and those which contain a group which is susceptible to a chemical reaction by which such functional groups are subsequently introduced to the *in situ*-formed polymer.

Alternatively, the polyelectrolyte or hydrogel may be formed in the pores of the substrate by, first, *in situ* polymerization of a monomer or a mixture of monomers, the monomer or at least one of the monomers of the monomer mixture being selected from those monomers which contain a functional group that provides an ion-exchange site and those which contain a group which is susceptible to a chemical reaction by which such functional groups are subsequently introduced to the *in situ*-formed polymer, and, subsequently, cross-linking the *in situ*-formed polymer.

The properties of the cross-linked polyelectrolyte or hydrogel located in the pores of the substrate, by covalent bonding to or cross-linked around structural elements of the porous substrate may be modified for specific applications by selection of the appropriate degree of cross-linking.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1, comprising graphs A and B, contains a graphical representation of the effects of temperature on pervaporation of water/ethanol mixtures, as detailed in Example 7 below.

GENERAL DESCRIPTION OF INVENTION

The porous microfiltration substrate which is modified to provide the charged membranes used herein

may comprise a porous substrate formed of polymeric material, such as polypropylene or polyethylene, into the pores of which may be *in situ* polymerized and cross-linked polyelectrolytes or hydrogels anchored to the substrate polymer by either covalent bonding to or cross-linked around the structural elements of the porous substrate.

For porous substrates, the pore diameters may vary widely but preferably range from about 0.01 to about 20 microns, more preferably from about 0.1 to about 5 microns and particularly from about 0.2 to about 1.0 microns. Pore diameters for microporous substrate are measured by the bubble-point method according to ASTM F-316.

The porosity or pore volume of a polymeric porous substrate used herein is preferably from about 25 to about 95%, more preferably from about 45 to about 85% and particularly from about 60 to about 80%. Porosity can be derived from the value of the bulk density of the porous substrate and the polymer density of substrate polymer according to ASTM D-792.

The thickness of substrate will depend on the intended use of the membrane product. For many uses, for example microfiltration, thicknesses ranging from about 1 to about 1000 microns, more preferably about 10 to about 240 microns and particularly about 20 to about 100 microns, would be suitable.

In situ polymerization of a suitable monomer to enable anchoring of polymeric molecules having ionizable groups may be effected by any convenient polymerization procedure, preferably by free-radical polymerization operation. Such free radical polymerization may include initiation of the polymerization by radiation initiation, thermal initiation or redox initiation. Typical initiators which may be used in the free radical polymerization include benzoin ethers and benzoyl

peroxide. The *in situ* polymerization may include graft polymerization.

Monomers which are suitable for such *in situ* polymerization include unsaturated derivatives containing a functional group that provides, or can be modified by a post-polymerization treatment to provide, an ion-exchange site to permit formation of a polyelectrolyte or hydrogel. The membrane which is formed may be anionic or cationic, depending on the unsaturated monomer which is *in situ* polymerized. Suitable examples include 4-vinylpyridine, acrylic acid, methacrylic acid, styrene, vinylbenzyl chloride and acrylamido-alkyl-sulfonic acid, such as 2-acrylamido-2-methyl-1-propane sulfonic acid. The polymers so formed in the pores are non-extractable therefrom and hence anchored therein.

The cross-linking of the *in-situ* polymerized molecule to control or modulate conformational flexibility of such molecules may be effected by adding the cross-linking monomer to the *in-situ* polymerized monomer, so that the *in-situ* polymerization and cross-linking occur simultaneously. Alternatively, the cross-linking may be effected as a separate operation following the initial *in-situ* polymerization. The cross-linking which is formed may be covalent or ionic in nature and may be effected by radiation cross-linking.

The simultaneous *in situ* polymerization and cross-linking is preferred since the yield of the *in-situ* polymerization in terms of increase over the base weight of the substrate, is significantly increased thereby.

The cross-linking agent may be any suitable unsaturated molecule capable of reacting to produce cross-links in the *in-situ* polymerized molecules. The cross-linking agent may be a molecule containing at least two unsaturated moieties to permit the formation

of cross-links. Examples of such monomers are divinylbenzene and divinylpyridine. Other examples of suitable cross-linking monomers are diacrylates, such as di(ethylene glycol) diacrylate, tetra(ethylene glycol) diacrylate or 1,6-hexanediol diacrylate.

The quantity of cross-linking monomer used depends on the membrane application and may vary up to about 30 wt% of the total weight of *in situ* polymerized monomer mixture. For water treatment under low pressure driven applications, the quantity of cross-linking monomer may run up to about 10%, preferably from about 0.25 to about 5 wt% of total weight *in situ* polymerized monomer mixture. For the electrodialysis, diffusion dialysis and Donnan dialysis applications, the quantity of cross-linking monomer may vary from about 0.25 to about 30 wt%, preferably from about 15 to about 25 wt% of total weight of *in situ* polymerized monomers.

The polyelectrolytes may be cross-linked after they have been formed *in situ* in the pores by a post-polymerization treatment. The cross-linking agent used in this type of post-polymerization cross-linking may be a molecule containing at least two or more functional groups capable of reacting with functional groups or other active sites on the *in situ* formed polymer to form covalent bonds or ionic bonds. Examples of molecules forming covalent bonds are dialkylating reagents, such as 1,3-dibromopropane, diacylating and triacylating reagents, such as isophthaloyl and trimesoyl chlorides, respectively. Examples of ionic cross-linking include complexes formed between multivalent transition metal ions and carboxylic acid groups.

The quantity of *in situ*-formed polymer depends on the membrane application and may vary from about 20 to about 400 wt% of the initial weight of the polymeric porous substrate. For water treatment under low pressure driven applications, the quantity of *in situ*-formed

polymer may vary from about 30 to about 200 wt%, preferably from about 45 to about 100 wt% of weight of the polymeric porous substrate. For electrodialysis, diffusion dialysis and Donnan dialysis applications, the quantity of *in situ*-formed polymer may vary from about 50 to about 250 wt%, preferably from about 150 to about 250 wt% of polymeric porous substrate.

The amine type nitrogen atoms of incorporated polymers may be quaternized for certain applications, such as by alkylation, for example, with dimethyl sulphate, as well as alkyl halides, including arylalkyl halides.

Particular combinations of monomers for production of the cross-linked polyelectrolyte or hydrogel which may be employed include:

- an *in-situ* formed copolymer of vinylpyridine and a monomer selected from divinyl benzene and divinylpyridine,
- an *in-situ* formed polyvinylpyridine which is subsequently cross-linked with an alkylating agent, such as 1,3-dibromo-propane,
- an *in-situ* copolymer of vinylbenzylchloride and divinylbenzene into which the ion-exchange functional groups are introduced by reaction with a tertiary amine,
- an *in-situ* formed copolymer of styrene and divinylbenzene into which the ion-exchange functional groups are introduced by sulfonation,
- an *in-situ* formed copolymer of acrylic acid or methacrylic acid and divinylbenzene,
- an *in-situ* formed copolymer of acrylic acid or methacrylic acid and a diacrylate.
- an *in-situ* formed copolymer of acrylic acid or methacrylic acid and tetra(ethyleneglycol) diacrylate.

- an *in-situ* formed copolymer of an 2-acrylamido 2-methyl-1-propane sulfonic acid and tetra(ethyleneglycol) diacrylate.

5 Microporous polypropylene or polyethylene membranes which have about 45 to about 100 wt% by weight of polymeric porous substrate of *in situ* polymerized vinylpyridine and which are cross-linked with about 0.25 to about 5 wt% by weight of the total monomers by divinylbenzene are particularly useful in pressure
10 driven water treatment, i.e. reverse osmosis or nanofiltration, possessing the property to reject multivalent cations in preference to monovalent cations. By varying the degree of the amount of the *in situ*-formed polymer and the degree and properties of the cross-linking, the membrane may be modified to be
15 specific for specific applications. For electrodialysis, diffusion dialysis and Donnan dialysis applications, microporous polypropylene or polyethylene membranes which have about 150 to about 250 wt% by weight of polymeric porous substrate of *in situ*
20 polymerized vinylpyridine and which are cross-linked with about 15 to about 25 wt% by total weight of the monomers by divinyl-benzene are particularly useful.

Ion rejection and use of charged membranes:

25 The charged membranes, comprising a non-ionic, porous substrate having pores which are filled with a cross-linked polyelectrolyte bound to or around the structural elements of the substrate polymer, are capable of rejecting both inorganic and organic ions
30 from water at pressures as low as 345 kPa (50 psig), a pressure which is within the range of tap water delivery pressure. Such preferential rejection is seen at even lower pressures down to 140 kPa (20 psig).

35 The rejection of salts containing monovalent cations, for example, Na^+ , is substantially lower than rejection of salts with multivalent cations, for

example, Mg^{2+} , Ca^{2+} . Charged organic materials, such as organic acids and salts, also are rejected by the membranes, while relatively large non-ionic organic molecules, such as sucrose, have low rejections by the membranes. The ability of the membranes to function at such ultra-low pressures and their distinctive pattern of separations distinguishes the membranes from commercially available nanofiltration or reverse osmosis membranes, which function only effectively at higher pressures and generally exhibit high rejections of large non-ionic organic molecules.

Unlike commercial membranes, the pore-filled membranes provided herein exhibit quite a different dependence of the ratio of permeate flux with a salt solution as feed to permeate flux with pure water as feed on pressure. At low pressures, a 0% DVB cross-linked grafted material has a permeate to pure water flux which exceeds 1. This ratio decreases with increasing pressure due either changes in the membrane itself or concentration polarization. With a 1% cross-linking, the ratio at low pressure is reduced somewhat below 1 but is essentially pressure independent. With 4% cross-linking, the membrane starts to behave much more like a typical commercial thin-film composite membrane.

The ability of the membranes provided herein to effect ultra-low pressure ion-rejection has wide application of use in water treatment technology to soften water without removing most non-ionic organic matter from water. Such applications may range from domestic water softening operations to the removal of calcium from tap water supplied to air conditioning systems as well as to water softening applications generally.

Existing commercial membranes used for water softening are limited by an excessive and indiscriminate

rejection of all dissolved species and this is particularly true with thin-film composite membranes, commercial examples being low-pressure nanofiltration membranes available from FilmTec and Fluid Systems. Other nanofiltration membranes which have been developed specifically for removal of organic materials from water, generally humic acid derivatives, exhibit a low removal of ions, including calcium. The recommended operating pressures for commercially available low pressure nanofiltration membranes are higher than those found to be sufficient for the invented membranes.

Diffusion Dialysis

The technologies currently employed for treating waste acid streams generally involve neutralization and solid waste disposal. The costs of such a disposal routine are increasing rapidly and environmental concerns and the value of recovering of a variety of metal ions, for example, chromium, are strong incentives for treatment of these waste streams.

The charged membranes provided herein are useful in diffusion dialysis of solutions containing mineral acids and metal salts to separate the salts from the acids, with the acids being transported through the membranes at high rates while the salts are rejected by the membranes. The degree of cross-linking employed in the membranes used in diffusion dialysis is generally greater than for pressure driven processes. The permeability of the membranes to protons is not much affected by cross-linking, up to a certain level. However, water permeability and metal ion permeability are affected. The membranes are also suitable for separating acids from neutral organic compounds under diffusion dialysis conditions.

Diffusion dialysis with the charged membranes can be used for the recovery of acid and stabilization of electrolyte composition in a number of industrial

processes, such as in the almite process, in aluminum capacitor etching, purification and metal salt recovery in non-ferrous smelting and refining, stabilization of electrolytic etching solutions and treatment of spent pickling solutions in secondary processing of iron and steel, and in purification of industrial acids, such as sulfuric acid and hydrochloric acid.

Electrochemical and related processes and uses of charged membranes

Charged membranes are used in a wide variety of electrochemical applications including electrodialysis, electrolysis, fuel cells and battery separators. A key feature of membranes for these applications are high ion-exchange capacities, low water transport, low electrical resistance, and good selectivity in terms of the transport of ions of different charge type (cations versus anions).

The charged membranes provided herein are useful in the applications, such as electrodialysis, electrochemical processes, fuel cells and batteries. In particular, they have very high ion-exchange capacities, exceeding 4 milli-equivalents per gram, and very low electrical resistances. The measured resistances are independent of cross-linking degree at least for the range of about 1 up to about 5 wt%, thereby allowing control over water permeability by using more highly cross-linked polyelectrolytes within the pores. Such membranes constitute a further aspect of the invention.

Pervaporation

Pervaporation is a process in which a liquid feed solution is placed in contact with a membrane on the other side of which is a vapor phase. Generally, the vapor phase is held at a partial vacuum. Components in the liquid phase are transported through the membrane, evaporate on the vapor side of the membrane and are subsequently condensed for recovery. Selectivity in

separation of the components in the feed is achieved by the proper choice of membrane material. Pervaporation is widely used in the final dehydration of ethanol.

5 The membranes provided herein are useful in pervaporation processes showing very high overall fluxes and good separations. They can be used, for example, in the purification of ethanol/water streams.

EXAMPLES

10 In the specific Examples which follow, polypropylene (PP) or polyethylene (PE) microporous substrates were used which had an average pore diameter of about 0.2 μm , a thickness of about 50 μm and a porosity of about 65 to 70 volume percent. Such polypropylene substrates were made following the
15 procedure described in U.S. Patent No. 4,726,989 (Marozinski) while the polyethylene substrates were made following the procedure described in U.S. Patent No. 4,539,265 (Shipman), the disclosures of such United States patents being incorporated herein by reference.

20 Example 1:

This Example illustrates the preparation of membranes.

The PP and PE substrates were subjected to *in situ* polymerization of 4-vinylpyridine (4VP) with varying
25 amounts of divinylbenzene (DVB) to provide anion-exchange membranes. Divinylbenzene of technical grade containing 55% of a mixture of monomers, was purchased from Aldrich Chemical Company, St. Louis, MO and was initially purified by vacuum distillation. All reagents
30 employed in the membrane preparations described herein were purchased from Aldrich Chemical Company.

A. Thermally-initiated *in situ* polymerization:

In thermally-initiated *in situ* polymerization from the vapor phase, the porous PP or PE substrate was
35 coated with benzoyl peroxide (BPO) by immersing it in an acetone solution containing 1% BPO and 1% poly(vinyl

acetate) for 5 to 10 minutes and subsequent drying it in air. The coated substrate was suspended inside a glass reactor containing on its bottom 2 to 3 mL of a vinylpyridine/DVB mixture. After the pressure inside the reactor had been reduced below 10 mmHg, the reactor was heated to 80°C for half an hour to effect the polymerization.

B. Photo-initiated *in situ* polymerization:

In photo-initiated *in situ* polymerization from solution, the porous PP or PE substrate was wetted with vinylpyridine, DVB and 1 to 1.5% of benzoin ethyl ether as a photo-initiator. The wetted substrate was degassed in a freeze-thaw cycle and irradiated using light of wavelength 350 nm for 30 minutes.

In each such procedure, unbound homopolymer was removed from the membranes by extraction with boiling methanol until no further mass loss occurred.

C. Quaternization:

Quaternization of amine groups in the *in situ* formed cross-linked polymer was effected by immersing the membrane into a solution containing 5 to 10% by volume of dimethyl sulfate in methanol at room temperature for 16 to 24 hours followed by subsequent thorough wash of the membrane with methanol and, finally, with deionized water. In an alternative procedure, the membrane was immersed into a solution containing about 5 wt% of dimethylsulfate in N,N-dimethyl-formamide at room temperature for 30 to 60 minutes followed by subsequent thorough wash of the membrane with deionized water.

D. Cross-linking with 1,3-dibromopropane:

Quaternization and cross-linking of amine groups in the *in situ* formed cross-linked polymer was effected with 1,3-dibromopropane carried out using a solution that contained 0.05 mol of 1,3-dibromopropane per 1 mol of pyridine nitrogen in the membrane dissolved in 100 to

150 mL of methanol. The membrane was placed in the solution and heated under reflux for 70 hours.

E. Cross-linking with α,α' -dibromo-p-xylene:

Quaternization and cross-linking of amine groups in the *in situ*-formed polymer was also carried out with α,α' -dibromo-p-xylene using a solution that contained 0.5 g of α,α' -dibromo-p-xylene in 80 mL of methanol. The ratio of α,α' -dibromo-p-xylene to pyridine nitrogen in the membrane was 5 to 1. The membrane was placed in the solution and heated under reflux for 16 hours.

Example 2

This Example shows the water softening capability of the membranes prepared as described in Example 1, in comparison to known membranes, as described by Fu et al., Journal AWWA, 86, 55 to 72 (1994).

A. Commercially-available membranes:

Four commercially-available thin-film composite membranes were tested for their ability to reject organic and inorganic components. Table I provides the chemical and physical characteristics of the membranes while Table II provides the performance data.

TABLE I

Characteristics of thin-film composite (TFC)
nanofiltration membranes

Membrane	Material	Rated Operating Pressure kPa (psig)	Flux at Rated Pressure L/m ² h (gpd/sq ft)	Permeability L/m ² h kPa (gpd/sq ft psig)
NF70 ⁽¹⁾	modified aromatic polyamide	483 (70)	37 (22)	0.118 (0.48)
TFCS ⁽²⁾	modified aromatic polyamide	552 (80)	26 (15)	0.049 (0.20)
NTR7450 ⁽³⁾	sulfonated polyether sulfone	986 (143)	93 (55)	0.106 (0.43)
NTR7410 ⁽³⁾	sulfonated polyether sulfone	986 (143)	496 (292)	0.185 (0.75)

- (1) FilmTec, Minneapolis, Minn.
 (2) Fluid Systems, San Diego, CA.
 (3) Nitto Denko from Hydranautics, San Diego, CA.

TABLE II

Rejection (%) of organics and inorganics by TFC nanofiltration membranes

Membrane	Color	TOC	Conductivity	Alkalinity	Calcium
NF70	> 97.5	94	90	93	98.5
TFCS	> 97.5	96	92	94	98.5
NTR7450	> 97.5	93	30	32	35.0
NTR7410	97.0	86	10	5	N/A

B. Membranes of Example 1:

(a) A membrane prepared as described in Example 1 by the photo-initiated *in-situ* polymerization procedure was tested for its water softening ability on untreated
5 tap water alone or in combination with organic materials at a flux of 2.52 L/m²h at 345 kPa (50 psig). The membrane was a polypropylene base membrane *in situ* polymerized with 4-vinylpyridine containing 1.2% divinylbenzene. This membrane was subsequently
10 quaternized by treatment with dimethyl sulphate as described in Example 1. The results obtained for individual runs of approximately 24 hours, which were reproducible over long term testing, are set forth in the following Table III:

TABLE III

COMPONENT	RUN 1 ⁽¹⁾		RUN 2 ⁽²⁾		RUN 3 ⁽³⁾	
	Feed, ppm	Rejection, %	Feed, ppm	Rejection, %	Feed, ppm	Rejection %
Sodium	19.5	71.3	13.3	38.8	13.3	60.0
Magnesium	12.0	97.4	10.4	58.6	8.9	91.0
Calcium	49.8	92.6	41.9	57.1	36.4	82.1
Acetate			115.8	48.2		
Chloride			16.9	51.0		
Sulfate			UD ⁽⁴⁾	99.5+		
Sucrose					558.4	12.9

Notes: (1) Run 1 = Tap water
 (2) Run 2 = Tap water + 100 ppm acetic acid
 (3) Run 3 = Tap water + 550 ppm sucrose
 (4) UD = undetectable due to precipitation of CaSO₄ at increased concentrations of Ca²⁺ in the feed.

As may be seen from these data, the charged membranes effected water softening since they remove calcium and other bivalent ions to a much larger extent than sodium ions. The results also show that the
5 membranes are able to remove charged organics (acetate).

Operation at 50 psig permits the membranes to be driven directly from a municipal water supply, with no pretreatment and with no additional pressurization being required and at pressures significantly lower than the
10 commercially-available membranes shown in Table 1 and 2.

(b) Two different membranes prepared as described in Example 1 by the thermally-initiated vapor phase *in situ* polymerization (Membrane A) and the photochemical *in situ* polymerization method (Membrane B) were tested
15 for their water-softening ability on untreated tap water. Membrane A was a polypropylene membrane *in situ* polymerized with 4-vinylpyridine containing 1.1 wt% of divinylbenzene. This membrane was subsequently quaternized by treatment with dimethyl sulphate as
20 described in Example 1. Membrane B was a polypropylene membrane *in situ* polymerized with 4-vinylpyridine containing 1.2 wt% divinylbenzene. This membrane was subsequently quaternized by treatment with dimethyl sulphate as described in Example 1 (same membrane as
25 Example 2(B)(a)).

The results are set forth in the following Table IV:

TABLE IV

Ion	Feed ppm	Membrane A Rejection % 345 kPa (50 psi)	Membrane A Rejection % 140 kPa (20 psi)	Membrane B Rejection % 345 kPa (50 psi)
Sodium	23.3	45.9	12.7	63.6
Magnesium	22.4	82.1	61.6	90.8
Calcium	85.5	66.4	29.7	88.4
Chloride	44.8	68.5	31.1	77.0
Sulphate	13.4	89.6	56.0	>99.5
Flux (L/m ² h)		5.76	2.12	2.52

These results show that substantial water softening is achieved at conventional tap pressures and that a pressure as low as 20 psi still provided substantial water softening.

5

Example 3

This Example illustrates the flux and rejection of cations from tap water using membranes prepared as described in Example 1.

10 Several different membranes, prepared following both the thermally-initiated and photoinitiated *in situ* polymerization procedures of Example 1, were tested for their flux and the ability to reject cations from tap water under a pressure of 345 kPa (50 psi). The results
15 obtained are summarized in the following Table V:

TABLE V

No.	Membrane Characteristics			Flux kg/m ² h	Rejection, %		
	Substrate	%DVB	Mass Gain, %		Na	Mg	Ca
Membranes prepared by photoinitiated polymerization							
1	PP	3.0	212.4	1.0- 1.7 ^a	51	68	56
2	PP	1.2	147.0	2.3	71	97	93
3	PP	0.5	60.5	4.1	40	65	59
4	PP	0.5	131.6	2.5	67	82	80
5	PP	0.3	124.7	4.1	47	60	60
6	PE	0.3	209.8	3.8	53	83	77
7	PE	0.00	67.5	11.5	6	8	8
Membranes prepared by thermally-initiated vapour-phase polymerization							
10	PP	1.0	350.9	5.5	62	85	80

Notes: ^a obtained with two samples prepared under identical conditions; measured under 1000 kPa and extrapolated to 345 kPa (50 psi)

As may be seen from the results set forth in the above Table V, membranes produced by photoinitiated polymerization exhibit several characteristics. By comparing experiments 3 and 4, it can be seen that the flux decreases with mass gain. Flux also decreases with increasing levels of cross-linking monomer (experiments 4 and 5). The separation level generally increases with increasing levels of cross-linking monomer. A trade-off exists among quantity of *in situ*-formed polymer, cross-linking, flux and separation. The polyethylene substrate produced membranes with higher fluxes than the polypropylene substrate for the same level of cross-linking and had a higher mass gain.

Example 4

This Example further illustrates the flux and rejection of cations from tap water using membranes prepared as described in Example 1 at a higher cross-linking and lower incorporation levels in comparison to Example 3.

A membrane was prepared generally following the photoinitiated *in situ* polymerization procedure of Example 1 to provide a polyethylene microporous membrane (PE) having a incorporation of 58% poly(4-vinylpyridine) cross-linked with 4% divinylbenzene and quaternized.

The membrane was prepared by a photochemical grafting (anchoring) procedure using 2,2-dimethoxy-2-phenylacetophenone as initiator. The contacting solution in the photografting was vinylpyridine with 4% divinylbenzene as a cross-linker diluted with pyridine, with the ratio of vinylpyridine/divinylbenzene to pyridine was 80:20. The presence of the pyridine leads to an improved uniformity in incorporation. The membrane was quaternized by treatment with dimethyl sulfate in dimethylformamide, which is a better solvent for nucleophilic substitution reactions than methanol and

allows not only to reduce the reaction time to less than an hour but also makes the reaction less sensitive to impurities, such as moisture.

5 Tests were conducted using this membrane at 500 kPa (72.5 psig) and converted to a temperature of 25°C for flux and the ability to reject cations from tap water and to reject sucrose from aqueous solution thereof. The membrane was cleaned by treatment with aqueous HCl (0.01M) after tap water tests and after sucrose tests,
10 which restored the properties of the membrane to their original values. The membrane was also tested at 345 kPa (50 psig) and 100 kPa (145 psig) on tap water. The results obtained at 500 kPa (72.5 psig) are outlined in the following Table VIA:

TABLE VIA

Feed	Flux (kg/m ² /h)	Separation Na ⁺ (%)	Separation Mg ²⁺	Separation Ca ²⁺	Separation Sucrose
De-ionized Water	41	-	-	-	-
54 ppm NaCl	48	62	-	-	-
109 ppm NaCl	52	43	-	-	-
Tap Water	46	26	36	36	-
60 ppm NaCl plus 547 ppm sucrose	41	49	-	-	12
De-ionized Water	43	-	-	-	-
126 ppm NaCl	43	41	-	-	-

The results obtained at 345 kPa (50 psig) and 100 kPa (14.5 psig) are set forth in the following Table VIB:

TABLE VIB

Pressure	Flux (kg/m ² /h)	Separation Na ⁺ (%)	Separation Mg ²⁺	Separation Ca ²⁺ (%)
345 kPa (50 psig)	36	26	38	37
100 kPa (14.5 psig)	12	9	30	28

As may be seen from the data presented in Tables VIA and VIB, using a microporous polyethylene substrate, the flux of the membrane has been increased in comparison to the results shown in Table V in Example 3. This result has been achieved by increasing the degree of cross-linking coupled with a decrease in the amount of material contained within the pores.

As compared to the results in Table V, there is some loss in separation which may be restored by increasing the loading, at the expense of flux. While fouling of the membrane occurred during the course of the experiments, the membranes were restored to their initial performance values by a simple dilute acid wash.

As may be seen from Table VIA, the tested membrane gave a very low separation of sucrose, confirming the data shown in Table III. This result contrasts with the results obtained under the same conditions using a typical commercial nano-filtration membrane (Osmonics BQ01 membrane), as set forth in the following Table VII:

TABLE VII

Feed	Flux (kg/m ² /h)	Separation Na ⁺ (%)	Separation Mg ²⁺	Separation Ca ²⁺	Separation Sucrose
De-ionized Water	39	-	-	-	-
54 ppm NaCl	46	83	-	-	-
109 ppm NaCl	48	68	-	-	-
Tap Water	33	19	27	31	-
60 ppm NaCl plus 547 ppm sucrose	31	51	-	-	61
De-ionized Water	28	-	-	-	-
126 ppm NaCl	27	28	-	-	-

As may be seen from the data in Table VII, a steady decline in flux occurred during the experiments, which was not restored by the cleaning cycle. As also may be seen, this commercial membrane had a high separation of sucrose in contrast to the results in Table VI, although in other respects the results are comparable.

A further comparison was made under the same process conditions with a Hydranautics nanofiltration prototype membrane (7450) and the results are set forth in the following Table VIII:

TABLE VIII

Feed	Flux (kg/m ² /h)	Separation Na ⁺ (%)	Separation Mg ²⁺	Separation Ca ²⁺	Separation Sucrose
De-ionized Water	14	-	-	-	-
54 ppm NaCl	14	86	-	-	-
109 ppm NaCl	14	77	-	-	-
Tap Water	14	33	65	68	-
60 ppm NaCl plus 547 ppm sucrose	15	72	-	-	97
De-ionized Water	16	-	-	-	-
126 ppm NaCl	15	58	-	-	-

As may be seen from the data in Table VIII, this membrane exhibits higher separation than achieved in Table VIA but at a substantially lower flux. A very high sucrose separation is marked contrast to the results of Table VIA. In addition, which the flux remained constant throughout the experiments, there was a loss of separation of NaCl with time and cleaning cycles did not restore the separation.

As may be seen from the data presented in this Example, the membranes used in accordance with the invention exhibited much better long term stability than the commercial membranes, comparable or better separations and quite different behaviour with sucrose/salt mixtures.

Example 5

This Example illustrates the use of the membranes for diffusion dialysis.

A membrane prepared as described in Example 1 comprising a polypropylene substrate having poly(4-vinylpyridine) (P4VP) and 3.3% DVB copolymerized in the pores thereof, was tested for diffusion dialysis of hydrochloric acid and sodium chloride in comparison to a commercially-available diffusion dialysis membrane Selemion DSV or AMV.

The results appear in the following Table IX:

TABLE IX

Membrane	Concentr. of Acid mol/L	Concentr. of Salt mol/L	Permeability, U, mol/(m ² h (mol/L))		U _{HCl} /U _{NaCl}
			HCl	NaCl	
Selemion DSV or AMV	0.1	0.05	1.1	0.025	44
Example 1	0.1	0.05	14.0	1.4	10

Selemion DSV is a commercially available diffusion dialysis membrane, one of the few on the market. As can clearly be seen from Table IX, the permeability for the membranes provided herein is nearly 1.4 orders of magnitude larger than that of the DSV membrane. The selectivity is poorer by a factor of 4 for the membrane provided herein.

Example 6

This Example illustrates the effect of changing the degree of cross linking introduced in the *in situ* polymerization as well as post-polymerization cross-linking with 1,3-dibromopropane on diffusion dialysis.

Membranes were prepared as in Example 1. The membrane listed as Membrane D in the following Table X was the same as Membrane C except for a post-polymerization treatment with 1,3-dibromopropane. Both membranes C and D had a polypropylene substrate with P4VP and 0.3 % DVB *in situ* copolymerized in the pores thereof. Membranes E and F had 1.1% and 2.2% DVB cross-linking.

The membranes C, D, E and F were tested for diffusion dialysis with hydrochloric acid and sodium chloride in a flow cell. The membranes C, D, E and F provided herein were compared with the commercially available Selemion AMV membrane. The results obtained are set forth in the following Table X:

TABLE X

Membrane	Concentr. of Acid mol/L	Concentr. of Salt mol/L	Permeability, U, mol/(m ² h (mol/L))		U _{HCl} /U _{NaCl}
			HCl	NaCl	
Selemion AMV	1.0	0.5	4.3	0.07	61
Membrane C	1.0	0.5	58	14	4
Membrane D	1.0	0.5	104	13	8
Membrane E	1.0	0.5	60	7	9
Membrane F	1.0	0.5	80	8	10

The data shown in Table X show that increased cross-linking (up to 2.2% of cross-linker) with DVB gives membranes with higher acid permeabilities with increased selectivity. The additional cross-linking 5 with dibromopropane further improves the membrane performance.

Example 7

This Example illustrates the effect of the concentration of cross-linker on selectivity and water 10 permeability in diffusion dialysis recovery of acid.

Membranes were prepared generally according to the procedure of Example 1 by absorbing a solution of 4-vinylpyridine and varying amount of divinylbenzene with 2,2-dimethoxy-2-phenylacetophenone as photoinitiator 15 into the polypropylene substrate and irradiating at 350 nm for approximately one hour.

Diffisuiou dialysis testing was performed using a stirred cell with a feed solution consisting of 1 M HCl, 0.5 M NaCl and 0.5 M MgCl₂ and a permeate cell initially 20 containing deionized water.

The results obtained are set forth in the following Table XI:

TABLE XI

Membrane	% Graft Yield	% DVB X-Linker	U(H ⁺) ^a	$\frac{U(H^+)^b}{U(Na^+)}$	$\frac{U(H^+)^b}{U(Mg^{2+})}$	Water Transport ^c	IEC (meq/g) ^d	Thickness (μm) ^e	IE Conc. (eq/L) ^f
422	147	0.54	45	8.8	20	0.2	4.53	131	2.2
406	157	1.3	45	9.5	26	0.5	4.37	107	2.5
415	173	2.5	40	11	31	0.3	4.7	120	2.8
412	172	4.1	33	13	51	0.3	4.8	96	3.3
417	182	6.1	34	13	47	0.3	4.3	94	3.6
407	47	4.1	47	6.6	13	0.1	2.2	69	1.3
408	52	4.1	47	6.7	12	0.3	2.4	71	1.3
426	191	4.1	35	13	42	0.5	4.4	99	3.2
421	210	4.1	37	13	41	0.3	4.41	106	3.2
420	203	4.0	37	13	41		4.88	102	2.9
428	181	8.3	32	16	64	0.3	3.97	96	3.5
431	201	15.4	23	16	152	0.15	3.81	89	4.5
432	208	24.8	16	35	378	0.08	351	71	5.3
412c	172	85% DBP ^g	23	36	294	0.2		74	
412f	172	95% DBX ^h	16	75	554	0.2		102	
Sel. DSV			5.9	100	2500	0.02		116	

^a U = permeability: mol/hr·m²·M^b Error ± 5 - 10%^c mL/hr·m²·M^d IEC = Ion Exchange Capacity, determined as in: A, M. Mika et al, J. Memb. Sci. 108, 1995, pp 37-56.^e Measured in 1 M HCl by pycnometry.^f IE Conc. = Ion Exchange Concentration as equivalents of determined nitrogen per litre of water in the membrane.^g DBP = 1,3-dibromopropane : percent additional crosslinking calculated from mass gain.^h DBX = α , α' -dibromo-p-xylene : percent additional crosslinking calculated from mass gain.

5 The results set forth in Table XI show that the membrane selectivity is enhanced and water permeability reduced by substantial increases in the degree of crosslinking. The membranes outperformed the commercial membrane, Selemion DSV.

Example 8

This Example provides the membrane electrical resistance of certain of the membranes provided herein.

10 The electrical properties of membranes prepared following the procedures of Example 1 were determined for various levels of cross-linking and compared with those of two commercial cation and anion exchange membranes, respectively Selemion CMV and AMV.

15 The results are contained in the following Table XII:

TABLE XII

Membrane Crosslinking %	Mass Gain % weight	Thickness μm	IEC meq/g	R/ Ω (Cell)
4.5	195	90	3.01	0.02
3.4	186	117	3.16	0.03
2.2	251	126	3.26	0.03
1.1	170	109	3.18	0.04
Selemon CMV		150	ca 1.5	0.18
Selemon AMV		150	ca 1.5	0.36

As may be seen from the above Table XII, the electrical resistance of the membrane is very low. The resistance of the membrane is, within the error limits of the measurements, independent of the degree of cross-linking. As water permeability decreases with increased cross-linking, it appears that membranes optimized for electrodialysis will have relatively high cross-linker ratios, since water transport is unwanted in electrodialysis and many other electrochemical operations.

Transference numbers (t_+ and t_-) of the membrane having 4.5% DVB cross-linked therein are compared with the Selemon AMV in the following Table XIII:

TABLE XIII

	t_+	t_-
4.5% DVB Membrane	< 0.2	> 0.8
Selemon AMV	< 0.06	> 0.94

The high t_+ and low t_- values for the membrane containing 4.5% DVB implies that the membrane exchanges anions and rejects cations to a large degree, which is borne out by the water softening data contained in Example 2.

Example 9

The Example shows the use of the membranes for pervaporation.

Using a membrane prepared as described in Example 1 containing 4.5% DVB, the pervaporation properties were measured using an aqueous solution of ethanol containing 4% ethanol. The effect of temperature on separation factor (i.e. water selectivity) and flux were determined and plotted graphically. These data appear in Figure 1.

As seen in graph A, the separation factor increased with temperature. As seen in graph B, the flux also increased with temperature.

The effect of ethanol concentration was also tested. The results obtained are shown in the following Table XIV:

TABLE XIV

Feed Solution	Temperature °C	Flux (kg/m ² h)	Separation Factor
4 wt% ethanol	50	0.3	4
85 wt% ethanol	50	2.4	11

Based on the results seen in Table XIV, it can be concluded that the membrane is water selective.

Example 10

5 This Example illustrates the preparation of cation-exchange membrane.

A. A first series of cation-exchange membranes was prepared using a polypropylene (PP) microporous substrate with a pore filler derived by photopolymerization of a 50 wt% methacrylic acid
10 solution in water using benzophenone as a photoinitiator, and employing either divinylbenzene or tetra(ethyleneglycol) diacrylate as a cross-linking agent, following the procedure of Example 1.

A first membrane (BT10) comprised poly(methacrylic
15 acid with 1% divinylbenzene and had an incorporation yield of 123%. This membrane was evaluated for the water-softening ability, as described in the following Example.

A second membrane (BT12) comprised poly(methacrylic
20 acid) with 2% tetra(ethyleneglycol) diacrylate and had an incorporation yield of 120%. The measured ion-exchange capacity was 5.5 meq/g.

B. A second series of cation-exchange membranes were prepared from a PP microporous substrate having
25 poly(2-acrylamido-2-methyl-1-propane sulphonic acid) anchored in the pores and lightly cross-linked with tetra(ethyleneglycol) diacrylate. The polymerizations were carried out in the pores of the substrate using 1 part of 2-acrylamido-2-methyl-1-propane dissolved in a
30 mixture of water (1 part) and methanol (1 part), the diacrylate cross-linker and benzophenone as photoinitiator. Incorporation yields ranged from 150 to 400%. The performance of one of these membranes having 4% cross linking, in pressure-driven water treatment was
35 examined, as outlined below.

Example 11

This Example illustrates the water softening capability of cation exchange membranes.

A. Membrane BT10, prepared as described in Example 10, was tested for the water softening ability on tap water at 354 kPa (50 psig) at a flux of 1.22 kg/m²h. the rejection achieved was as follows:

	Na ⁺	16%
	Mg ⁺⁺	61%
10	Ca ⁺⁺	65%
	Cl ⁻	5%
	SO ₄ ⁻	42%

The separations which were achieved using the cation-exchange membrane based on poly(methacrylic acid) are comparable to those achieved using the anion-exchange membranes based on poly(4-vinylpyridine) at comparable fluxes.

B. Membrane BT16, prepared as described in Example 10, was tested for its water softening ability at 345 kPa (50 psig) in the treatment of tap water and in single salt separations at 483 kPa (70 psig). The rejection achieved on tap water (50 psig) at a flux rate of 1.9 kg/m²h was as follows:

	Na ⁺	14%
25	Mg ⁺⁺	29%
	Ca ⁺⁺	31%
	Cl ⁻	20%
	SO ₄ ⁻	51%

The results obtained for single salt separations (70 psig) are set forth in the following Table XV:

TABLE XV

SALT (0.002M)	FLUX (KG/M ² H. AT 70 PSIG)	REJECTION
NaCl	2.95	65
CaCl ₂	2.7	19
NaSO ₄	3.17	93

The fluxes achieved with these cation-exchange membranes were high and comparable to the poly(vinylpyridine) based membranes. The pattern of separations observed with the single salts in Table XV 5 was that expected for a negatively-charged membrane.

SUMMARY OF DISCLOSURE

In summary of this disclosure, the present invention provides membranes having unique properties in 10 a variety of applications. Modifications are possible within the scope of this invention.

CLAIMS

What we claim is:

1. In a membrane separation process selected from the group consisting of pressure driven membrane separation, diffusion dialysis, Donnan dialysis, electrodialysis, electrochemical synthesis, and pervaporation, the improvement which comprises employing a charged membrane comprising a porous substrate and a cross-linked polyelectrolyte or hydrogel located in the pores of the substrate.
2. The process of claim 1 wherein said membrane comprises a microporous substrate and about 20 to about 400 wt% weight of microporous substrate of a cross-linked in-situ polymerized polyelectrolyte or hydrogel located in the pores of the substrate and cross-linked by up to about 30 wt% of the polymerized monomers in the polyelectrolyte or hydrogel.
3. The process of claim 1 wherein said membrane separation process comprises a pressure-driven membrane separation to effect selective removal of multivalent cations from an aqueous medium containing monovalent cations and multivalent cations.
4. The process of claim 2 wherein, in said microporous membrane, the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 30 to about 200 wt% and the amount of cross-linking monomer is up to about 10 wt% of the in-situ polymerized monomers.
5. The process of claim 4 wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 45 to about 100 wt% and the amount of cross-linking monomers is about 0.25 to about 5 wt%.
6. The process of claim 2 which is effected at a pressure of 70 psig (500 kPa) or less.
7. The process of claim 6 wherein said membrane comprises a microporous substrate in the pores of which is *in situ* polymerized from about 45 to about 100 wt% of

the substrate of vinylpyridine which is cross-linked with from about 0.25 to about 5 wt% of total monomers by divinylbenzene.

8. The process of claim 7 wherein amine groups in the polyelectrolyte are quaternized.

9. The process of claim 1 wherein said membrane separation process comprises electrodialysis, diffusion dialysis or Donnan dialysis and wherein, in said microporous membrane, the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 50 to about 250 wt% and the amount of cross-linking monomers is from about 0.25 to about 30 wt% of the in-situ polymerized monomers.

10. The process of claim 9 wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 150 to about 250 wt% and the amount of cross-linking monomers is about 15 to about 25 wt%.

11. The process of claim 1 wherein said membrane separation process comprises electrodialysis, diffusion dialysis or Donnan Dialysis and wherein said microporous membrane comprises a microporous substrate having about 150 to about 250 wt% of the substrate of a cross-linked polyelectrolyte or hydrogel located in the pores of the substrate, said polyelectrolyte or hydrogel being polymerized 4-vinylpyridine which is cross-linked with about 15 to about 25 wt% of total polymerized monomers in said polyelectrolyte or hydrogel, by divinylbenzene and exhibiting a low electrical resistance and a low water permeability.

12. The process of claim 1 wherein the polyelectrolyte or hydrogel is formed in the pores of the substrate by *in situ* polymerization of a monomer or a mixture of monomers with a cross-linking agent, the monomer or at least one of the monomers of the monomer mixture being selected from those monomers which contain a functional group that provides an ion-exchange site and those which

contain a group which is susceptible to a reaction by which such functional groups are subsequently introduced to *in situ*-formed polymer.

13. The process of claim 1 wherein the polyelectrolyte or hydrogel is formed in the pores of substrate by, first, *in situ* polymerization of a monomer or a mixture of monomers, the monomer or at least one of the monomers of the monomer mixture being selected from those monomers which contain a functional group that provides an ion-exchange site and those which contain a group which is susceptible to a chemical reaction by which such functional groups are subsequently introduced to the *in situ*-formed polymer, and, subsequently, cross-linking *in situ*-formed polymer.

14. The process of claim 1 wherein the polyelectrolyte is a copolymer of vinylpyridine and a monomer selected from divinylbenzene and divinylpyridine.

15. The process of claim 13 wherein the polyelectrolyte is polyvinylpyridine cross-linked with a dialkylating reagent after *in situ* polymerization.

16. The process of claim 15 wherein said dialkylating agent is 1,3-dibromopropane or α,α' -dibromo-*p*-xylene.

17. The process of claim 14 wherein the polyvinylpyridine is quaternized with an alkyl or aryl substituted alkyl halide or sulphate.

18. The process of claim 1 wherein the polyelectrolyte is selected from the group consisting of (1) copolymers of vinylbenzyl chloride and divinylbenzene and the ion-exchange functional groups are introduced by reaction with a tertiary amine; (2) copolymers of styrene and divinylbenzene and the ion-exchange functional groups are introduced by sulfonation; (3) copolymers of acrylic acid and divinylbenzene; (4) copolymers of methacrylic acid and divinylbenzene; (5) copolymers of acrylic acid and a diacrylate; or (6) copolymers of methacrylic acid and a diacrylate.

19. The process of claim 1 wherein the substrate is a microporous polyolefin substrate.
20. The process of claim 19 wherein the polyolefin is polypropylene or polyethylene.
21. The process of claim 1 wherein the properties of the bound polyelectrolyte or hydrogel are modified for a specific membrane and separation process by selection of the degree and type of cross-linking of the polyelectrolyte or hydrogel.
22. A charged membrane comprising a microporous polypropylene or polyethylene substrate and about 45 to about 100 wt% of a cross-linked polyelectrolyte or hydrogel located in the porous of the substrate, said cross-linked polyelectrolyte or hydrogel being polymerized 4-vinylpyridine which is cross-linked with from about 0.25 to about 5 wt% of total polymerized monomers in said polyelectrolyte by divinylbenzene.
23. The charged membrane of claim 22 wherein amine groups in said polyelectrolyte or hydrogel are quaternized by reaction with a quaternizing agent.
24. The charged membrane of claim 23 wherein said quaternizing agent is an alkyl or arylalkyl halide or a sulphate.
25. The charged membrane of claim 24 wherein said quaternizing agent is dimethyl sulphate.
26. A charged membrane comprising a microporous polypropylene or polyethylene substrate and a cross-linked polyelectrolyte or hydrogel located in the pores thereof which is further cross-linked by reaction with a cross-linking agent.
27. The charged membrane of claim 26 wherein said cross-linking agent is 1,3-dibromopropane or α,α' -dibromo-p-xylene.
28. The charged membrane of claim 26 wherein said cross-linked polyelectrolyte or hydrogel is a copolymer of vinylpyridine and a monomer selected from

divinylbenzene and divinylpyridine.

29. The charged membrane of claim 28 wherein amine groups in said polyelectrolyte or hydrogel are quaternized.

30. The charged membrane of claim 29 wherein said amine groups are quaternized by reaction with dimethylsulphate.

31. A charged membrane comprising a microporous polypropylene or polyethylene substrate and about 150 to about 250 wt% of the substrate of a cross-linked polyelectrolyte or hydrogel located in the pores of the substrate, said polyelectrolyte or hydrogel being polymerized 4-vinylpyridine which is cross-linked with about 15 to about 25 wt% of total polymerized monomers in said polyelectrolyte or hydrogel, by divinylbenzene and exhibiting a low electrical resistance and a low water permeability.

32. The charged membrane of claim 31 wherein said cross-linked polyelectrolyte or hydrogen is a copolymer of vinylpyridine and a monomer selected from divinylbenzene and divinylpyridine.

33. The charged membrane of claim 31 wherein said polymerized 4-vinylpyridine is quaternized.

34. The charged membrane of claim 33 wherein said polymerized 4-vinylpyridine is quaternized with dimethylsulphate.

35. A charged membrane comprising a microporous substrate and about 20 to about 400 wt% weight of microporous substrate of a cross-linked in-situ polymerized polyelectrolyte or hydrogel located in the pores of the substrate and cross-linked by up to about 30 wt% of the polymerized monomers in the polyelectrolyte or hydrogel.

36. The charged membrane of claim 35 which is suitable for water treatment applications wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about

30 to about 200 wt% and the amount of cross-linking monomer is up to about 10 wt% of the in-situ polymerized monomers.

37. The charged membrane of claim 36 wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 45 to about 100 wt% and the amount of cross-linking monomers is about 0.25 to about 5 wt%.

38. The charged membrane of claim 35 which is suitable for electrodialysis, diffusion dialysis and Donnan dialysis applications wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 50 to about 250 wt% and the amount of cross-linking monomers is from about 0.25 to about 30 wt% of the in-situ polymerized monomers.

39. The charged membrane of claim 38 wherein the quantity of in-situ polymerized polyelectrolyte or hydrogel is about 150 to about 250 wt% and the amount of cross-linking monomers is about 15 to about 25 wt%.

1/1

Pervaporation with Water/Ethanol Mixtures:
Effect of Temperature

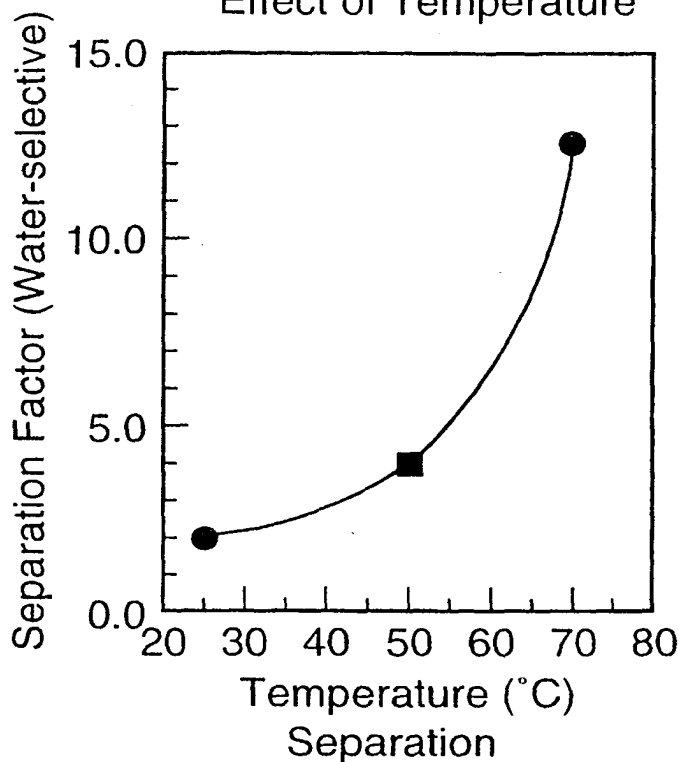


FIG.1A

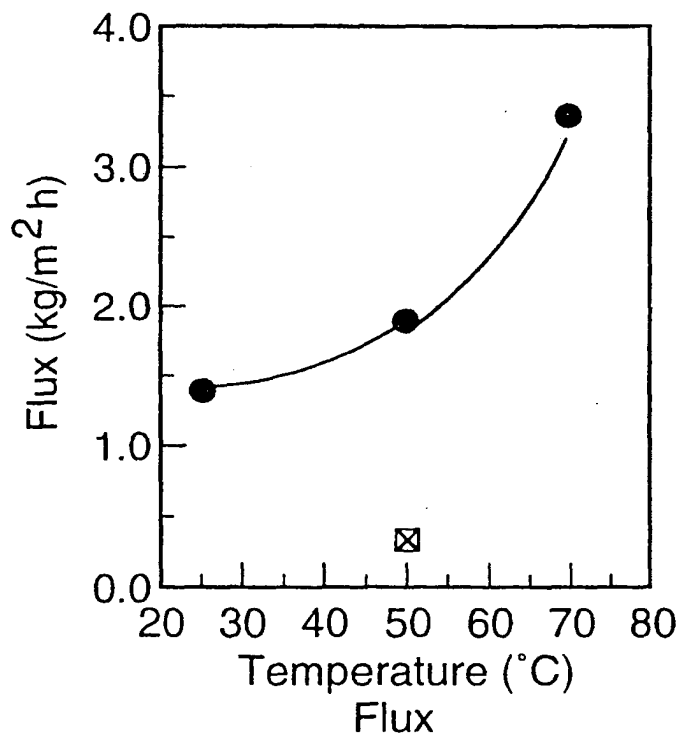


FIG.1B

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 97/00770

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01D69/10 B01D69/14 B01D67/00 B01D71/28 B01D71/78
B01D71/80 B01D71/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 97 17129 A (UNIV TOLEDO) 15 May 1997 see page 8, line 5 - page 8, line 13 see page 8, line 21 - page 9, line 15; claim 1 --- -/--	1,18-20, 26,35,36

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

13 February 1998

Date of mailing of the international search report

27.02.98.

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Edmüller, P

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 97/00770

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 049 275 A (GILLBERG-LAFORCE GUNILLA E ET AL) 17 September 1991</p> <p>see column 3, line 26 - column 3, line 68 see column 4, line 24 - column 4, line 38 see column 5, line 17 - column 5, line 41 see column 6, line 3 - column 6, line 46 see column 9, line 49 - column 10, line 14 see column 10, line 56 - column 10, line 64; claims 1,5,7,8,19,20,29-32; examples 8-50,56</p> <p>---</p>	<p>1-7, 9-14, 18-22, 28,31, 32,35-39</p>
X	<p>EP 0 474 617 A (MONSANTO CO) 11 March 1992</p> <p>see page 3, line 17 - page 3, line 34 see page 4, line 22 - page 5, line 47; claims 1-6; table 1</p> <p>---</p>	<p>1,2,4,7, 9-14, 18-20, 22,26, 31,32, 35-39</p>
X	<p>EP 0 309 259 A (TOA NENRYO KOGYO KK) 29 March 1989</p> <p>see page 2, line 3 - page 2, line 7 see page 3, line 3 - page 3, line 16 see page 4, line 13 - page 4, line 22 see page 6, line 6 - page 6, line 10 see page 6, line 23 - page 6, line 26; claims 12,14,15,17</p> <p>---</p>	<p>1,3, 18-21, 26,35-39</p>
X	<p>WO 92 05595 A (SCIMAT LTD) 2 April 1992</p> <p>see page 3, paragraph 3 - page 5 see page 7, paragraph 1 - page 9, line 4 see page 17, line 1 - page 20, line 1</p> <p>---</p>	<p>1,2,4,5, 7,12,14, 18-22, 26,28, 31,32, 35-39</p>
X	<p>WO 87 06395 A (RAYCHEM LTD) 22 October 1987</p> <p>see page 1, paragraph 1 see page 5, paragraph 4 - page 7; claims 1,10; examples 1,2,4-6</p> <p>---</p> <p>---/---</p>	<p>1,2,4,5, 12, 18-21, 26,35-39</p>

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	<p>WO 91 10498 A (GELMAN SCIENCES INC) 25 July 1991</p> <p>see page 8, line 18 - page 9, line 23; examples 10-12</p> <p style="text-align: center;">---</p>	<p>1,26, 35-39</p>
A	<p>JOURNAL OF MEMBRANE SCIENCE, vol. 108, 1995, page 37-56 XP002055563 cited in the application</p> <p style="text-align: center;">-----</p>	<p>1-39</p>

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(51) International Patent Classification⁶ : B01D 69/10, 69/14, 67/00, 71/28, 71/78, 71/80, 71/82	A1	(11) International Publication Number: WO 98/17377 (43) International Publication Date: 30 April 1998 (30.04.98)
(21) International Application Number: PCT/CA97/00770 (22) International Filing Date: 17 October 1997 (17.10.97) (30) Priority Data: 08/733,792 18 October 1996 (18.10.96) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/733,792 (CIP) Filed on 18 October 1996 (18.10.96) (71) Applicant (for all designated States except US): McMASTER UNIVERSITY [CA/CA]; 1280 Main Street West, Hamilton, Ontario L8S 4M1 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): MIKA, Alicja, M. [PL/CA]; 25 Brodrick Street, Hamilton, Ontario L8S 3E3 (CA). CHILDS, Ronald, F. [CA/CA]; 130 Grant Boulevard, Dundas, Ontario L9H 6J4 (CA). DICKSON, James, M. [CA/CA]; 111 Hillcrest Avenue, Hamilton, Ontario L8P 2X1 (CA).		(74) Agent: STEWART, Michael, I.; Sim & McBurney, 6th floor, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MICROPOROUS MEMBRANES AND USES THEREOF (57) Abstract <p>Charged membranes comprise a porous substrate and a cross-linked polyelectrolyte or hydrogel located in the pores of the substrate and are useful in a variety of membrane separation processes, including pressure driven membrane separation, diffusion dialysis, Donnan dialysis, electrodialysis, electrochemical synthesis and pervaporation.</p>		

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